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Recovery of phenolic compounds from orange press liquor by nanofiltration

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ABSTRACT

This research was undertaken in order to evaluate the potential of a nanofiltration (NF) process for the separation and concentration of phenolic compounds from press liquors obtained by pigmented orange peels. Four different spiral-wound NF membranes, characterised by different molecular weight cut-off (MWCO) (250, 300, 400 and 1000 Da) and polymeric material (polyamide, polypiperazine amide and polyethersulphone), were investigated. The rejection of the investigated membranes towards anthocyanins, flavonoids and sugars was evaluated in order to identify a suitable membrane to separate phenolic compounds from sugars. The performance of the investigated NF membranes was also evaluated in terms of permeate flux and antifouling performance.

The obtained results indicated a reduction of the average rejection towards sugars by increasing the MWCO of the selected membranes, while the rejection towards anthocyanins remained higher than 89% for all the NF membranes investigated. The NFPES10 membrane showed the lowest average rejection towards sugar compounds and high rejections towards anthocyanins (89.2%) and flavonoids (70%). Permeate flux values at lower transmembrane pressures were also favourably high compared to the other NF membranes.

Keywords: Citrus press liquors; Nanofiltration; Flavonoids; Anthocyanins

1. Introduction

Citrus fruits are widely used in food industries for producing fresh juice, citrus-based drinks and cans (Spiegel-Roy and Goldschmidt, 1996). Since the juice yield is less than half of the fruit weight a large quantity of by-products such as peel, seeds, cells and membrane residues are produced every year. These by-products are traditionally used for the production of molasses, pectins, essential oils, limonene and cattle feed. Moreover, citrus by-products are enriched in bioactive compounds, such as flavonoids and phenolic acids, recognised for their beneficial implications in human health due to their antioxidant activity and free radical scavenging ability (Anagnostopoulou et al., 2006). The recovery of these compounds offers new opportunities for the formulation of products of interest in food (dietary supplements and functional foods production), pharmaceutical (products with antibacterial, antiviral, anti-inflammatory, antiallergic and vasodilatory action) and cosmetic industry (Benavente-Garcia et al., 1997).

Several extraction techniques have been proposed for the extraction of phenols from citrus peels including solvent extraction (Li et al., 2006a), γ-irradiation-assisted extraction (Oufedjikh et al., 2000), ultrasound-assisted extraction (Ma et al., 2009), heat treatment (Xu et al., 2007), enzyme-assisted extraction (Li et al., 2006b), supercritical fluid extraction (Giannuzzo et al., 2003), resin-based extraction (Di Mauro et al., 2000) and alkaline extraction (Bocco et al., 1998).

These extraction methods are characterised by some drawbacks, such as the degradation of the compounds of interest due to high temperatures and long extraction times (as in solvent extractions) and health-related risks. Medical interest in drugs obtained from plants has led to an increased need for ideal extraction methods, which could obtain the maximum of the bioactive constituents in a shorter processing time with a low cost. Besides, recent interest in anthocyanins has arisen not only due to their potential health benefits but also to their use as natural colorants (Zhang et al., 2004).

Recently, membrane technology has attracted attention as an alternative molecular separation technology.

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Nomenclature

A	membrane area (m^2)
C_{pa}	solute concentration in accumulated permeate at the end (ppm)
C_f	solute concentration in the feed (ppm)
C_r	solute concentration in the retentate (ppm)
FI	fouling index (%)
J_p	permeate flux (L/m^2 h)
MWCO	molecular weight cut-off (Da)
NF	nanofiltration
PWP_a	pure water permeability after filtration (L/m^2 h)
PWP_b	pure water permeability before filtration (L/m^2 h)
R	rejection (%)
t	filtration time (h)
T	temperature (°C)
TMP	transmembrane pressure (bar)
UF	ultrafiltration
V_f	feed volume (L)
V_p	permeate volume (L)
V_r	retentate volume (L)
VRF	volume reduction factor

Compared to the traditional methods used for the extraction of polyphenols, membrane technologies offer new possibilities due to their advantages in terms of high recovery or removal efficiency, low energy input, mild operating conditions, absence of phase transition and easy integration with other operating units. In particular, nanofiltration (NF), the most recently developed pressure-driven membrane process for liquid-phase separations, has been found to be extremely efficient in the fractionation and concentration of solutes from complex solutions. It offers higher fluxes than reverse osmosis and better retention than ultrafiltration for lower molar mass molecules such as sugars, natural organic matters and ions.

The main advantage of employing NF membranes for the purification of natural compounds is that by selecting membranes with suitable molecular weight cut-off (MWCO), this technology can be used to fractionate molecules of similar molecular weight (150–1000 Da range).

In recent years, a large number of potential applications of NF has been proposed. Mello et al. (2010) investigated the concentration of propolis extracts using water and ethanol as solvents by NF; for aqueous solutions, the NF membrane retained around 94% of phenolic compounds and 99% of flavonoids showing high efficiency in the concentration of propolis extracts. Biologically active compounds extracted from *Sideritis scardica Grisep*, an endemic plant of the Balkan Peninsula, were also concentrated by NF membranes resistant to organic solvents (Tylkowski et al., 2011).

Diaz-Reínoso et al. (2009) processed an aqueous extract from pressed distilled grape pomace by ultrafiltration (UF) and NF membranes to obtain fractions enriched in compounds having antioxidant activity. An UF-NF integrated membrane process was also proposed by Cissé et al. (2011) for the concentration of anthocyanins from roselle extract.

Up to now no information is available on the performance of NF membranes in the treatment of by-products of citrus processing. The present work was undertaken in order to evaluate the potential of NF membranes in the separation and concentration of bioactive compounds from press liquors obtained by pigmented orange peels. In particular, the rejection of different NF membranes towards anthocyanins, flavonoids and sugars was evaluated in order to identify a suitable membrane to separate phenolic compounds from sugars. The performance of the investigated NF membranes was also evaluated in terms of permeate flux and antifouling performance.

Table 1 – Composition of the orange press liquor.

pH	3.4 ± 0.04
Sugars (°Brix)	9.6 ± 0.1
Flavonoids (mg/L)	1974.1 ± 25.6
Anthocyanins (mg/L)	194.1 ± 16.8
Ca^{++} (mg/L)	398.1 ± 7.9
Mg^{++} (mg/L)	150.1 ± 3.0

2. Materials and methods

2.1. Orange press liquor

The orange press liquor coming from blood orange peel processing was supplied by Citrech Snc (Messina, Italy). It was stored at −17 °C and defrosted at room temperature before use.

The main components of the press liquor used as raw material for NF experiments are presented in Table 1.

2.2. Experimental set-up and procedures

NF experimental runs were performed by using a laboratory plant supplied by Matrix Desalination Inc. (Florida, USA) (Fig. 1). The equipment consists of a feed tank with a capacity of 12 L, a stainless steel housing for 2.4 × 21 in. spiral-wound membrane module, a high pressure pump, a back-pressure valve, two pressure gauges, a permeate flowmeter and a permeate tank. A cooling coil, fed with tap water, was used in the feed tank to control the feed temperature.

Four spiral-wound NF membrane modules were selected on the basis of their particular MWCO and materials: N30F and NFPES10, supplied by Mycrodin Nadir, and NF70 and NF200, supplied by Filmtec/Dow. Properties of these membranes, obtained from manufacturers' data sheet, are summarised in Table 2.

All experiments were performed according to the batch concentration configuration in which the permeate is collected separately and the retentate is recycled to the feed tank.

Experimental trials with NF70 and NF200 membranes were carried out at a transmembrane pressure (TMP) of 20 bar and at a temperature of 20 °C; N30F and NFPES10 membranes were operated at TMP and temperature values of 6 bar and 20 °C, respectively. Volume permeation fluxes were measured up to a volume reduction factor (VRF) of 3. The VRF was defined as the ratio between the initial feed volume and the volume of the resulting retentate according to the following equation (Garcia-Castello et al., 2011):

$$\mathrm{VRF} = \frac{V_f}{V_r} = 1 + \frac{V_p}{V_r} \quad (1)$$

where V_f, V_p and V_r are the volumes of feed, permeate and retentate, respectively.

Three different parameters were used to characterise the membrane performance: the permeate flux, the solute rejection and the fouling index.

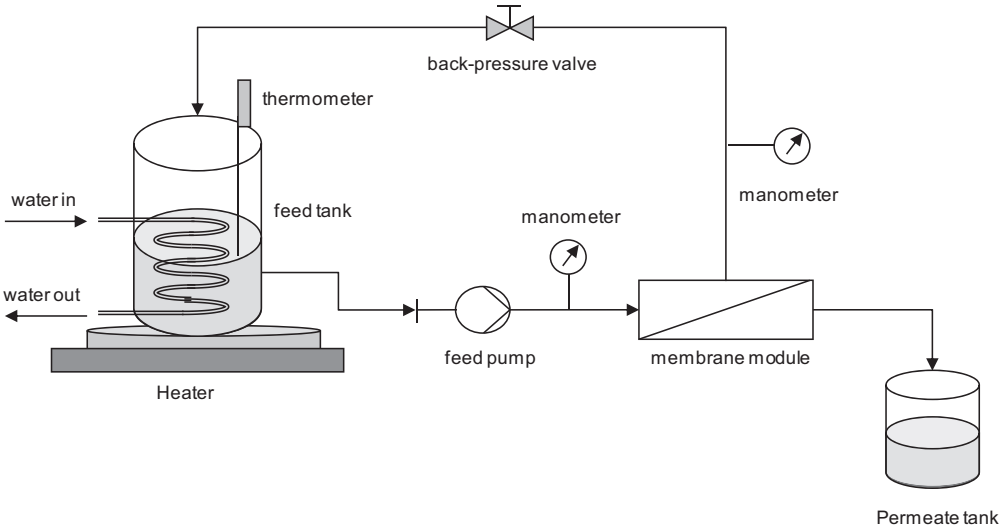

Fig. 1 – Schematic diagram of the NF experimental setup.

The average permeate flux (J) was determined by measuring the collected permeate volume in a given time through the membrane surface area, at constant values of TMP and temperature, by using the following equation:

$$J = \frac{V_p}{At} \quad (2)$$

where V_p is the volume permeated through the membrane of surface area A in time t. The rejection (R) of NF membranes towards specific compounds was calculated as:

$$R = \left(1 - \frac{C_{pa}}{(C_f + C_r)/2}\right) \times 100 \quad (3)$$

where C_{pa} is the concentration in accumulated permeate at the end, C_f the concentration in the feed at the beginning and C_r the concentration in the residual concentrate at the end.

The fouling index (FI) of NF membranes was calculated by comparing the pure water permeability before and after the press liquor filtration (Mänttäri and Nyström, 2007) according to the following equation:

$$FI = \left(1 - \frac{PWP_a}{PWP_b}\right) \times 100 \quad (4)$$

where PWP_b and PWF_a are the pure water permeability before and after the press liquor filtration.

The water permeability of each membrane was determined by the slope of the straight line obtained by plotting the water flux values, measured in fixed conditions of temperature (25 °C), versus the applied TMP.

After the treatment with orange press liquor, NF membranes were rinsed with tap water for 30 min and their pure water permeability was measured; then, the fouled membranes were submitted to a cleaning procedure by using a 0.125 M NaOH solution, at 40 °C for 60 min. At the end of the chemical cleaning procedure, the pure water permeability was measured again.

Experimental runs were performed in triplicate. Permeate flux data were expressed as mean ± SD.

2.3. *Analytical measurements*

Samples of feed, permeate and retentate were analysed for total flavonoids, anthocyanins content, sugars and calcium and magnesium salts.

Total flavonoids were measured by using a modified colorimetric method (Yuan et al., 1996). Properly diluted press liquor samples (0.5 mL) were added to a test tube containing 3.5 mL of absolute ethanol. After addition of 4 mL of 90% diethylene glycol and thorough mixing, the reaction was initiated by adding

Table 2 – Properties of 2.5 × 40 in. spiral-wound NF membranes.

Membrane type	NF-70	NF-200	N30F	NFPES10
Manufacturer	Dow/Filmtec	Dow/Filmtec	Microdyn Nadir	Microdyn Nadir
Material	0.2 μm crosslinked aromatic polyamide + 0.46 μm polysulfone	Polypiperazine amide thin-film composite	Polyethersulfone	Polyethersulfone
NMWCO (Da)	180	300	400	1000
Membrane surface area (m^2)	2.1	2.6	1.6	1.6
Maximum operating pressure (bar)	41	41	40	40
Maximum operating temperature (°C)	45	45	50	50
NaCl retention (%)	70	–	25–35	5–15
Na_2SO_4 retention (%)	–	–	85–95	25–40
$CaCl_2$ retention (%)	85–95	35–50	–	–
$MgSO_4$ retention (%)	95	>97	–	–
pH range	2–11	3–10	2–11	2–11
Membrane charge at neutral pH	Negative	Negative	Negative	Negative

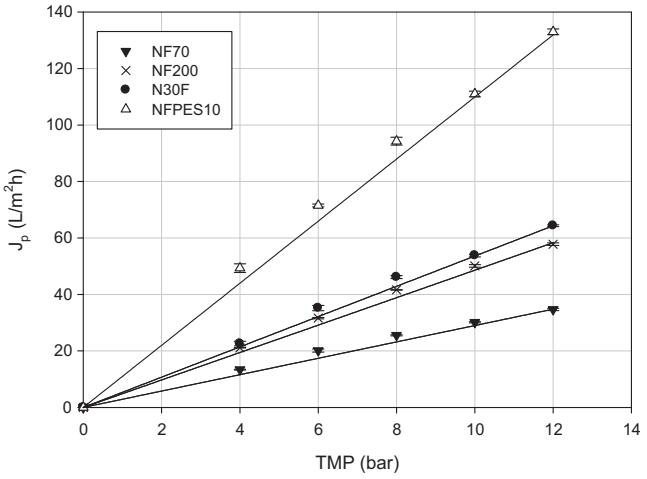

Fig. 2 – Permeate flux variation with TMP for different NF membranes using deionised water ($T = 25\,^{\circ}C$).

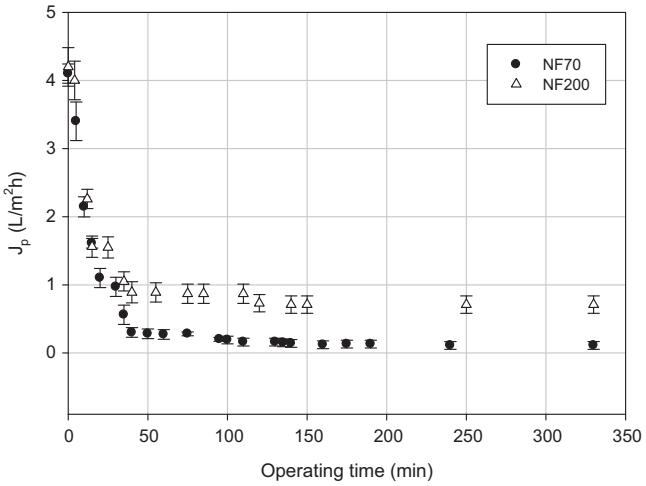

Fig. 3 – Treatment of orange press liquors with NF70 and NF200 membranes. Permeate flux as a function of processing time (TMP = 20 bar, $T = 20\,^{\circ}C$).

0.1 mL of 4 M NaOH. Absorbance at 420 nm was measured after 10 min of incubation at 40 °C using an UV-Vis recording spectrophotometer (UV-160 A, Shimadzu Scientific Instruments, Inc., Japan). Hesperidin was used as the standard and total flavonoids content was expressed as mg hesperidin/L.

Anthocyanins were determined by a colorimetric method (Francis, 1982): 5 mL samples of press liquor was mixed with 45 mL of a EtOH/HCl solution prepared by mixing 79.3 mL of anhydrous ethyl alcohol with 20.3 mL of HCl (37%). The absorbance was measured at 535 nm. The calibration curve was obtained by measuring the absorbance of standard solutions of pure cyanidin-3 glucoside. The anthocyanin concentrations were calculated using the extinction coefficient 1018.3 at 535 nm.

The sugar content, expressed in °Brix, was measured by using an Abbe-60/DR refractometer (Bellingham & Stanley Ltd., London, UK) at 20 °C.

The calcium and magnesium contents were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Optima 2100 DV-Perkin Elmer) operating in the axial viewing mode (Dean and Ma, 2008). Argon, air and nitrogen were the gases used. 10 mL of each sample was dried at 500 °C. The ashes were dissolved in 10 mL of HCl and 1 mL of HNO_3 and double-distilled water added to give a final volume of 50 mL. The blank for the analysis was prepared by adding HNO_3 to distilled water to give a final concentration of 2% (v/v). Similarly, before measurements, samples and standard Ca^{++} and Mg^{++} solutions were acidified with HNO_3 in order to obtain a final solution containing HNO_3 at 2% (v/v). The emission wavelength for calcium and magnesium was 317.9 nm and 285.2 nm, respectively. All measurements were performed in triplicate. Results were expressed as mean ± SD.

3. Results and discussion

3.1. *Water permeability of NF membranes*

Fig. 2 shows the permeate flux variation with TMP for different NF membranes using pure water. The results show that J_w increases linearly with TMP over the range of TMP values investigated (0–12 bar). In general, an increase in the hydraulic permeability is observed by increasing the MWCO, because larger pore sizes lead to higher pure water fluxes. However, it must be noted that water permeability is also affected by the internal structure of the membrane; therefore, other factors in addition to MWCO, such as morphology and hydrophobicity/hydrophilicity, also influence the value.

3.2. *Treatment of orange press liquor*

Figs. 3 and 4 show the time course of permeate flux observed for the selected NF membranes at a temperature of 20 °C up to a VRF of 3.

The initial permeate flux of NF70 and NF200 membranes was about 4.1 L/m^2 h at a TMP of 20 bar; however, the NF 200 membrane showed a higher steady-state permeate flux, for the same operating conditions. This phenomenon can be attributed to the higher MWCO of the NF 200 membrane.

N30F and NFPES10 membranes showed a better performance at lower TMP (6 bar); in particular, the initial permeate flux of the N30F membrane was about 4.6 L/m^2 h, while for the NFPES10 membrane the initial permeate flux was 10.4 L/m^2 h; steady-state permeate fluxes were 2.1 and 3.4 L/m^2 h, respectively.

The antifouling performance of a membrane is one of the most important factors to be considered in selecting a membrane for a specific application because membrane fouling

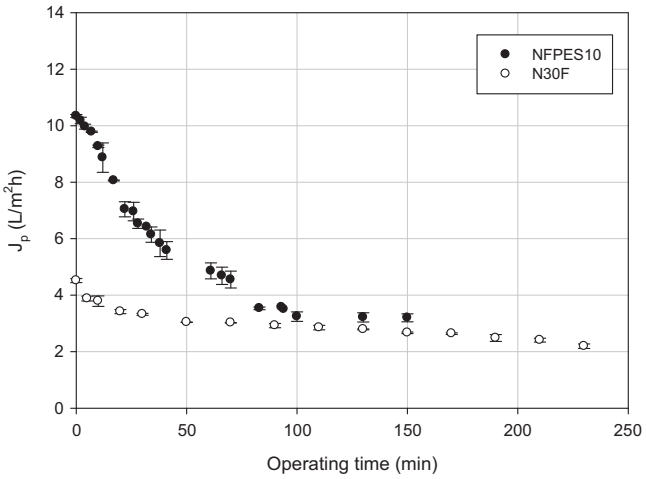

Fig. 4 – Treatment of orange press liquors with N30F and NF PES10 membranes. Permeate flux as a function of processing time (TMP = 6 bar, $T = 20\,^{\circ}C$).

Table 3 – Pure water permeabilities before (PWP_b) and after (PWP_a) filtration of press liquors with NF membranes and calculated fouling indexes.

	Membrane type			
	NF70	NF200	N30F	NFPES10
PWP_b (L/m^2 h bar)	3.05	5.07	5.57	11.30
PWP_a (L/m^2 h bar)	2.68	4.36	1.39	2.96
Fouling index (%)	12.10	14.00	75.04	73.80

manifests itself as a decline in flux with time of operation reducing productivity and shorting membrane life (Nilsson, 1990). It is a complex phenomenon depending on specific membrane–solution interactions and caused by the deposition of small colloidal particles on the inner walls of the membrane pores (standard blocking), the blocking of the membrane pore openings (complete blocking) and the build up of particles in the form of a cake layer (Mousa and Al-Hitmi, 2007).

In Table 3 water permeabilities of NF membranes before and after the filtration of press liquor are reported. The *FI* for the NF 200 membrane was 14%, the lowest among the four NF membranes, exhibiting the best anti-fouling performance. The higher *FI* values for the N30F and NFPES10 membranes (75.04 and 73.80, respectively) can be attributed to the higher hydrophobicity of the polyethersulphone (PES) membranes. Boussu et al. (2006) reported contact angle values of 72° and 88° for NFPES10 and N30F, respectively, indicating the N30F membrane to be the most hydrophobic. This is in agreement with the highest *FI* observed for this membrane.

Similar results have been reported by Susanto et al. (2009), who investigated on the adsorption of polyphenols from green tea on the surface and inside PES membranes. According to Susanto et al. (2009) the adsorptive fouling of polyphenols on PES membranes is influenced by the pore size, polar interactions (van der Waals, electron donor–acceptor interaction) and multiple hydrogen bonds towards the additive polyvinylpyrrolidone (PVP) in PES. An increase of both adsorbed amount and affinity for polyphenol binding to PES with increasing PVP content has been also reported by Cartalade and Vernhet (2006). In addition, mixtures of polyphenols with other components, such as polysaccharides, could form aggregates having a strong contribution to adsorptive fouling of PES membranes (Ulbricht et al., 2009).

The membrane water permeability of N30F membrane dropped by 24.2% after the liquor treatment; a complete recovery (99%) of the hydraulic permeability was obtained after cleaning with NaOH (Fig. 5a). For the NFPES10 membrane, rinsing with water recovered 63% of the initial water permeability due to the removal of the concentration polarisation layer; with chemical cleaning, 83.4% of the initial water permeability was recovered, confirming the presence of a fouling resistance probably due to the adsorption of materials which cannot be removed by the conditions employed in this work. By contrast, the water permeability of both NF 200 and NF 70 membranes was completely restored after the cleaning with water (Fig. 5b). Simões Couto et al. (2011) found similar results in the evaluation of NF membranes for the retention of anthocyanins of acai juice. In particular, composite membranes composed of a polyamide top layer and a polysulphone microporous support, like the NF 70 membrane, presented the highest water permeability before and after NF processing of acai juice.

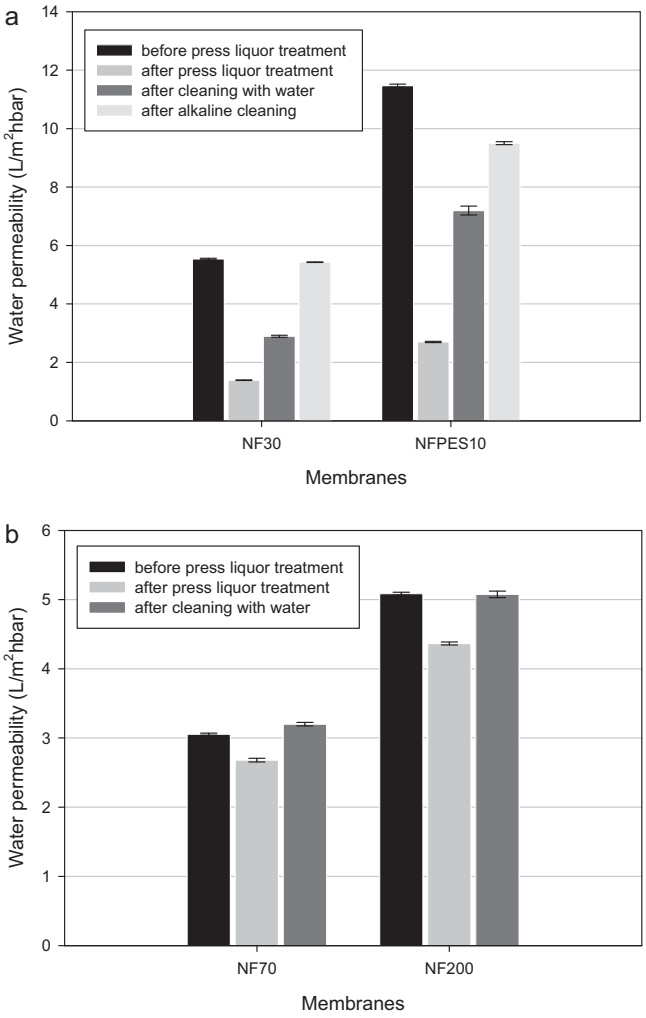

Fig. 5 – Water permeability of NF membranes before and after cleaning procedures: (a) N30F, NFPES10; (b) NF200, NF 70.

3.3. *Analytical results*

Table 4 shows the composition of press liquor, permeate and retentate streams in terms of sugars, flavonoids and anthocyanins for all the NF membranes investigated. The initial feed showed a content of anthocyanins similar to that reported by Mondello et al. (2000) in the blood orange juices of the cultivar Moro.

Fig. 6 shows the average rejection of NF membranes towards the flavonoids, anthocyanins and sugars. All the NF membranes investigated presented high average rejections towards anthocyanins (in the range 89.2–95.9%) and flavonoids (in the range 70.0–95.4%). Sugar compounds were weakly retained by the NFPES10 membrane (22.8%) and strongly retained by the NF70 membrane.

In particular, the NF 70 membrane, with the lowest NMCO, showed the highest average rejection towards flavonoids and anthocyanins (95.4% and 95.9%, respectively). These results are very similar to those reported by Cissé et al. (2011) in their NF treatment of clarified roselle extract with the same membrane. The average rejection towards sugars was 93.4%. The NF 200 membrane retained all flavonoids and anthocyanins in the retentate side (rejection of 88.4 and 94.2% towards flavonoids and anthocyanins, respectively); in contrast, about 30% of sugars were measured in the permeate stream. The PES membranes (N30F and NFPES10) showed low average rejections

Table 4 – Analytical determination of sugars, flavonoids and anthocyanins in feed, permeate and retentate streams coming from the NF treatment of press liquors (average values of three samples ± standard deviation).

Membrane type	Sample	Flavonoids (ppm)[a]	Anthocyanins (ppm)[b]	Sugars (°Brix)
NF70	Feed	1950.0 ± 7.5	199.6 ± 4.4	9.0 ± 0.1
	Permeate	111.4 ± 5.0	10.8 ± 0.2	0.8 ± 0.1
	Retentate	2908.6 ± 10.0	326.9 ± 13.0	15.4 ± 0.1
NF200	Feed	1971.4 ± 8.0	140.5 ± 3.2	9.0 ± 0.1
	Permeate	397.1 ± 5.5	14.5 ± 0.3	4.8 ± 0.1
	Retentate	4890.2 ± 11.0	359.6 ± 8.0	22.8 ± 0.1
N30F	Feed	2001.4 ± 8.5	207.4 ± 6.0	11.0 ± 0.1
	Permeate	561.4 ± 6.5	23.4 ± 0.1	8.0 ± 0.1
	Retentate	4410.3 ± 9.5	509.2 ± 7.0	17.0 ± 0.1
NFPES10	Feed	2204.3 ± 11.0	175.1 ± 2.3	10.0 ± 0.1
	Permeate	1011.4 ± 7.0	34.6 ± 0.5	9.8 ± 0.1
	Retentate	4395.6 ± 10.5	465.4 ± 3.5	15.4 ± 0.1

[a] Hesperidin equivalents.
[b] Cyanidin-3 glucoside equivalents.

towards sugars. The average rejection of the N30F membrane towards sugar compounds was 42.8%, while for the NFPES10 was 22.8%. Thus the use of the NFPES10 membrane for concentration of the press liquor led to a certain recovery of sugars in the permeate stream, indicating that this membrane offered the best separation of phenolic compounds from sugars.

The high rejection towards phenolic compounds obtained with both PES membranes is in agreement with the higher IF observed in comparison with the other NF membranes investigated.

Basically, the rejection of NF membranes towards the analysed compounds decreased by increasing the MWCO of the selected membranes (Fig. 7). However, the rejection of all selected membranes towards anthocyanins was higher than 89%. This behaviour can be explained assuming that anthocyanins, unlike other subgroups of flavonoids with a similar C6-C3-C6 skeleton, have a positive charge in their structure at acidic pH (the pH of the orange press liquor is 3.4). At this pH the selected membranes exhibit a positive charge; in particular, Boussu et al. (2008) reported a zeta potential of 1 mV at pH 3 for N30F and NFPES10 membranes. Consequently, the electrostatic repulsion, independent of the MWCO of the selected NF membranes, contributes to the high average rejection of the membranes towards anthocyanins.

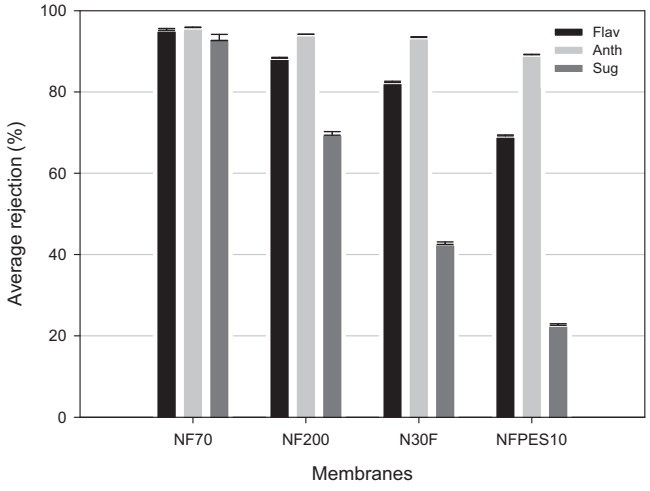

Fig. 6 – Average rejection values of NF membranes towards sugars, flavonoids and anthocyanins.

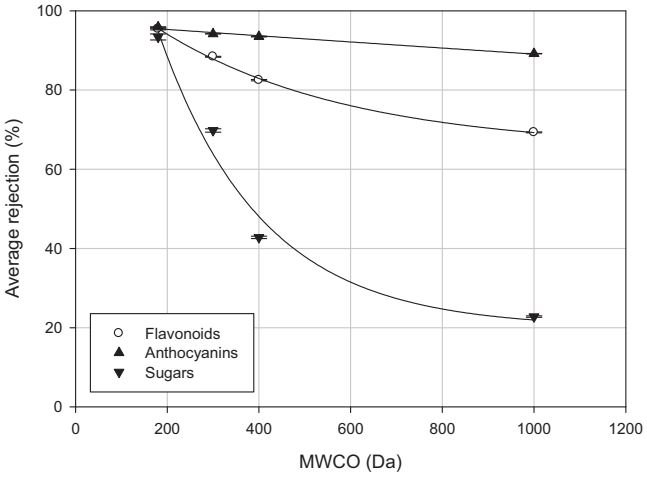

Fig. 7 – Average rejection values of flavonoids, anthocyanins and sugars as a function of MWCO.

Table 5 shows the composition of press liquor, permeate and retentate streams in terms of calcium and magnesium salts for all the NF membranes investigated. The average rejection of NF membranes towards these salts is reported in Fig. 8. Looking at the MWCO of NF70 and NF200 membranes it becomes clear that these NF membranes have rather small

Table 5 – Determination of calcium and magnesium in feed, permeate and retentate streams coming from the NF treatment of press liquors (average values of three samples ± standard deviation).

Membrane type	Sample	Ca (ppm)	Mg (ppm)
NF70	Feed	376.0 ± 7.5	143.0 ± 2.8
	Permeate	24.5 ± 0.5	8.4 ± 0.1
	Retentate	771.0 ± 15.4	248.0 ± 5.0
NF200	Feed	394.7 ± 5.6	132.0 ± 2.6
	Permeate	24.6 ± 0.4	8.1 ± 0.2
	Retentate	1018.0 ± 20.4	376.0 ± 7.5
N30F	Feed	485.6 ± 9.7	193.0 ± 3.8
	Permeate	225.5 ± 4.5	127.8 ± 2.6
	Retentate	1129.1 ± 22.6	394.8 ± 7.9
NFPES10	Feed	423.7 ± 8.5	175.3 ± 3.5
	Permeate	293.8 ± 5.9	124.7 ± 2.5
	Retentate	1055.0 ± 21.1	367.0 ± 7.1

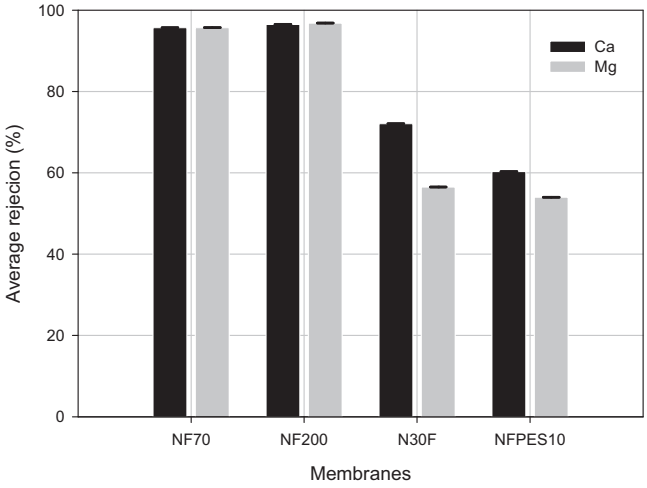

Fig. 8 – Rejection values of NF membranes towards Ca^{++} and Mg^{++} salts.

pores, situated near the reverse osmosis end of the NF region. The pores are too small to see only a charge effect, which explains the high retention of Ca^{++} and Mg^{++} ions.

4. Conclusions

The performance of four spiral-wound NF membranes in the separation and concentration of flavonoids from press liquors obtained from pigmented orange peels was evaluated.

A strong reduction of the average rejection towards sugar compounds was observed by increasing the MWCO of the selected membranes while for anthocyanins rejections were higher than 89%, independent of pore size.

The NFPES10 membrane gave the lowest average rejection towards sugar compounds and high rejections towards both anthocyanins (89.2%) and flavonoids (70%). Initial permeate flux values at lower transmembrane pressures were also higher than the other NF membranes investigated. The use of NF PES10 membrane for concentrating press liquor allows recovery of some sugars in the permeate stream, yielding the best separation of phenolic compounds from sugars. The hydrophobic character of the PES membranes accounts for the high fouling index measured for these membranes (about 74%). An incomplete recovery of the initial water permeability was also observed after alkaline cleaning with NaOH, indicating that fouling had occurred, which could not be removed by the cleaning protocols used here.

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